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Direct observation of Schottky to ohmic transition in Al-diamond contacts using real-time photoelectron spectroscopy*

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Abstract

Real-time photoelectron spectroscopy and in-situ electrical measurements have been applied to the formation of Al contacts on p-type diamond. At 294 K, an initially uniform Al film induces band-bending in the diamond consistent with the measured (current-voltage) barrier height of 1.05 V. The temperature-induced transition to an ohmic contact has been monitored in real-time revealing a direct correlation between the onset of surface bonding at 755 K and an abrupt change in surface band-bending. The reaction temperature is lower than previously believed and there is a second transition point at 1020 K where the rate of change of both reaction and band-bending increases sharply.

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The quality of synthetic diamond single-crystals has dramatically improved in recent years and is now enabling applications of this wide-gap semiconductor in electronic and optoelectronic devices [1]. Although there are many remaining issues regarding bulk quality (e.g. defects, dopants), the ultimate device performance is also limited by electron transport across heterointerfaces. For example, the degree of rectification of a metal-semiconductor diode is rarely predictable, and diamond is no exception.[2,3] However, diamond shows important differences to other, structurally similar semiconductors: there is a more pronounced metal-dependence with an S-parameter of up to 0.6 [3] and the rectification shows a strong dependence on surface morphology,[4] surface termination[5,6], interface oxides,[7] interface chemistry,[3,5] temperature[3,8] and substrate doping[9].

In order to untangle these influences, we have focused on Al contacts to single-crystal p-type diamond using a combination of spectroscopic and electrical transport techniques applied in parallel, in-situ and, for spectroscopy, in real-time. As this is the contact of choice for many device applications there is a decent body of literature, but there is considerable disagreement on even the most basic parameter, the Schottky barrier height: values of between 0.8 and 2.2 V have been reported using a range of methods for variously-prepared contacts.[3,5,7,10-13] There is also inconsistency in the influence of temperature on these contacts – an important consideration for high-temperature application of diamond electronics. For example, some studies report on stable rectification at temperatures up to 700 K[8,14] while others have observed ohmic behavior at such temperatures.[4] While there is agreement that Al contacts (in elemental or alloy form) can be used to fabricate ohmic contacts if annealed there is less agreement on the temperature required to achieve this. [3,4,15]

To minimize the influence of surface preparation, ambient conditions and temperature, all fabrication and measurements were carried out in a ultrahigh vacuum system ($p = 2 \times 10^{-10}$ mbar) equipped with fast x-ray photoelectron spectroscopy (XPS), low energy electron

diffraction (LEED), current-voltage (I-V) measurement, metallization and programmable temperature-profiling. A polished/acid-cleaned B-doped (001) CVD single crystal ($7.5 \times 7.5 \times 1.5$ mm^3, $N_B = 2 \times 10^{16}$ cm^{-3}) provided by Element Six Ltd. was used as the substrate for these studies. This surface was smooth to < 0.2 nm as determined by AFM measurements. Prior to metallization, the diamond was heated to 1100 K to remove surface contaminants. A 1×1 LEED pattern was observed for this clean surface and XPS measurements showed a single C1s peak with sub-monolayer residual oxygen. Al overlayers and metal contacts were produced by exposure to a calibrated Knudsen cell with a deposition rate of around 0.2 nm min^{-1}.

A comparison of the I-V characteristics for three selected contacts is shown in Fig. 1. The rectifying contacts (A, B) were fabricated using a shadow mask containing 1 mm diameter apertures; curve A was obtained by in-situ measurement and curve B was obtained by ex-situ measurement. The I-V characteristic of contact A was analyzed using thermionic emission theory to yield a barrier height of 1.05 eV with an ideality factor of 1.4, as shown in the right hand panel of Figure 1. This value is within the range of published values for this contact.[2,7] No diode measured ex-situ had an ideality factor better than 2 and so no reliable barrier height could be extracted from these data. A comparison of curves A and B illustrates the influence of oxygen on diode characteristics even for contacts prepared in an identical way in ultrahigh vacuum. The presence of oxygen is known to influence diode performance[7] and this preparation-dependence may account for some of the variation in barrier height reported for metal- diamond contacts. Contact (C) is non-rectifying (sheet resistance ~20 kΩ) and was prepared by heating small metallized regions to around 1100 K.

To study the transition between A and C by in-vacuo annealing, temperature-programmed, real-time photoelectron spectroscopy has been applied. Although XPS is a widely used method to study surface processes[16] the normal data acquisition time limits its

capability for probing the kinetics of interface formation. Advances in electron detector technology[17-19] are however enabling XPS spectra to be recorded at rates of around 1Hz or higher, but all studies to date have used synchrotron radiation as the photoexcitation source, and most have focused on adsorbate-induced chemical changes occurring at the monolayer level. The sensitivity of the Aberystwyth detector[17] allows the use of a lower intensity laboratory (Mg Kα) x-ray source.

A time sequence of C 1s photoelectron emission spectra is shown in Fig. 2, each recorded in 1s snapshot mode (without scanning the photoelectron energy) during exposure of a clean diamond surface to a flux of Al. The initial attenuation of the C 1s peak is consistent with uniform metal film growth (yielding an electron escape depth of ~1.2 nm). The persistence of this peak at longer exposure suggests subsequent cluster formation (Stranski-Krastanov growth mode). The profile of the clean surface C 1s spectrum remains unaffected by the metal overlayer, confirming the absence of strong interfacial bonding. The peak position however, changes significantly on metallization, moving by 0.26 eV to higher binding energy. This corresponds to an increase in band-bending in the p-type diamond (in addition to the initial band-bending for this surface,[6]) and is consistent with the formation of a rectifying contact as measured by I-V.

The temperature-dependence of the Al-diamond interface was probed in real-time by recording the C 1s core level in snapshot mode (10s per spectrum) during a programmed temperature ramping from 294 K to 1130 K at a rate of around 1.3 Ks^{-1} (Fig. 3). There are complex changes in intensity, peak shape and peak position during this annealing cycle. An initial increase in the diamond C 1s peak intensity due to enhanced metal clustering is followed, at higher temperatures, by a decrease in intensity as bulk Al-C chemical interaction dominates. The formation of new chemical bonds is confirmed by additional emission in the C 1s spectra at lower binding energy (higher kinetic energy). The energy position of the

diamond C 1s component reflects changes in the diamond Fermi level position relative to the band edges and this was also found to be temperature dependent. Quantitative information that enables the bonding and band-bending to be directly correlated is obtained by curve-fitting each of the spectra in Fig. 3. The fitting parameters were obtained from energy-scanned C 1s spectra recorded at selected stages of contact formation as shown in the inset of Fig. 4. Spectrum (a) represents a clean diamond surface, spectrum (b) represents an Al-covered surface and spectrum (c) represents a contact heated to above 1100 K and recorded at 294 K. The data points are shown along with fitted curves (solid lines) generated using lorentzian-gaussian mix functions. The clean surface and the Al-covered surface are fitted with two components: the dominant C1s bulk diamond (I) and a smaller (< 3%) surface component displaced by ~1 eV from the bulk peak. Following annealing, new carbide-related features become apparent (peak II), centered at around 2.8 eV lower binding energy compared to peak I. In each case the diamond component has a fitted width of 0.92 – 0.99 eV, typical for clean diamond surfaces[16]. The diamond C 1s peak (I) is shifted to higher binding energy upon metallization (spectrum (b)) but shifts by 0.52 eV to lower binding energy upon annealing (spectrum (c)) indicating decreased band-bending as the ohmic contact is formed. Fast XPS allows the transition between (b) and (c) to be monitored in real-time.

The kinetics of the temperature-induced changes are represented in Figure 4 by the peak position of the diamond C 1s peak (open triangles) and the peak intensities of both carbon species (open circles for peak I (diamond) and filled squares for peak II (carbide)). The data are extracted from 1 s snapshots and the solid line through the data points correspond to a 10 s averaging of the data points. Up to 755 K, there is little change in peak intensity, but there is a small, reversible, shift in peak position that reflects a temperature-dependent Fermi level. This phenomenon is believed to reflect the low density of states at the diamond surface even in the presence of a metal overlayer. An abrupt change is apparent in

the peak position (open triangles) of the diamond C1s component at 755 K. This is the onset of the transition from Schottky to ohmic behavior in the Al-diamond contact and it occurs at a lower temperature than previously believed for high-quality substrates and is lower even than the carbide onset temperature reported for Ti on diamond[20]. This first transition point is directly correlated with the onset of carbide formation as determined from the intensity of the low binding energy C 1s emission (peak II: filled squares). Metal clustering is also initiated around this temperature as evidenced from the increase in the diamond C 1s intensity (Peak I: open circles) as the Al atoms become mobile and the substrate becomes more exposed.

A second transition point occurs at 1020 K where the intensity of the substrate diamond component falls rapidly as the formation of bulk carbide dominates. This is accompanied by a sharp increase in the intensity of the carbide peak. At the same point, there is an increase in the rate of Fermi level shift (open triangles) towards the final position corresponding to a reduced interfacial barrier. This can be explained by the generation of new interface states within the band gap as the chemical interaction proceeds. The gap states that define the Fermi level position (and hence barrier height) are thus highly dependent on, and correlated with, the interfacial chemistry. In the lowest temperature range (294 K – 755 K), the density of gap states is low enough to show a reversible temperature-dependent shift. Between 755 K and 1020 K, the formation of Al-C bonds at the surface induce a higher density of states that moves the Fermi level closer to the valence band maximum, reducing the interfacial barrier. Above 1020 K, bulk carbide (Al_3C_4) formation accelerates the Fermi level shift and drives the contact irreversibly towards ohmic behavior.

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References

[1] D. J. Twitchen, A. J. Whitehead, S. E. Coe, J. Isberg, J. Hammersberg, T. Wikstrom, and E. Johansson, IEEE Trans. Electron Devices **51** (5), 826 (2004).

[2] H. Kawarada, Surf. Sci. Rep. **26** (7), 205 (1996).

[3] Y. G. Chen, M. Ogura, and H. Okushi, J Vac Sci Technol B **22** (4), 2084 (2004).

[4] T. Tachibana and J. T. Glass, J. Appl. Phys. **72** (12), 5912 (1992).

[5] F. Maier, M. Riedel, J. Ristein, and L. Ley, Diam Rel Mater **10** (3-7), 506 (2001).

[6] C. Saby and P. Muret, Diam Rel Mater **11** (3-6), 851 (2002).

[7] H. Kiyota, E. Matsushima, K. Sato, H. Okushi, T. Ando, M. Kamo, Y. Sato, and M. Lida, Appl Phys Lett **67** (24), 3596 (1995).

[8] C. A. Hewett and J. R. Zeidler, Diam Rel Mater **2** (10), 1319 (1993).

[9] H. Shiomi, Y. Nishibayashi, and N. Fujimori, Jpn. J. Appl. Phys. Part 1 **30** (7), 1363 (1991).

[10] C. A. Mead and T. C. McGill, Phys. Lett. A **58** (4), 249 (1976).

[11] M. C. Hicks, C. R. Wronski, S. A. Grot, G. S. Gildenblat, A. R. Badzian, T. Badzian, and R. Messier, J. Appl. Phys. **65** (5), 2139 (1989).

[12] F. J. Himpsel, P. Heimann, and D. E. Eastman, Solid State Commun. **36** (7), 631 (1980).

[13] D. Takeuchi, S. Yamanaka, H. Watanabe, H. Okushi, and K. Kajimura, Appl. Surf. Sci. **159**, 572 (2000).

[14] S. S. M. Chan, C. Peucheret, R. D. McKeag, R. B. Jackman, C. Johnston, and P. R. Chalker, J. Appl. Phys. **78** (4), 2877 (1995).

[15] H. J. Looi, L. Y. S. Pang, M. D. Whitfield, J. S. Foord, and R. B. Jackman, Diam Rel Mater **9** (3-6), 975 (2000).

[16] S. Evans, in *The Properties of Natural and Synthetic Diamond*, ed. J.E. Field, (Academic Press, London, 1992), pp.181-214.

[17] D. P. Langstaff, A. Bushell, T. Chase, and D. A. Evans, Nucl Inst Meth B **238** (1-4), 219 (2005).

[18] L. Gregoratti, A. Barinov, E. Benfatto, G. Cautero, C. Fava, P. Lacovig, D. Lonza, M. Kiskinova, R. Tommasini, S. Mahl, and W. Heichler, Rev. Sci. Instrum. **75** (1), 64 (2004).

[19] A. Nambu, J.-M. Bussat, M. West, B. C. Sell, M. Watanabe, A. W. Kay, N. Mannella, B. A. Ludewigt, M. Press, B. Turko, G. Meddeler, G. Zizka, H. Spieler, H. van der Lippe, P. Denes, T. Ohta, Z. Hussain, and C. S. Fadley, J. Electron Spectrosc. Relat. Phenom. **137-140**, 691 (2004).

[20] P. E. Viljoen, E. S. Lambers, and P. H. Holloway, J Vac Sci Technol B **12** (5), 2997 (1994).

Figures

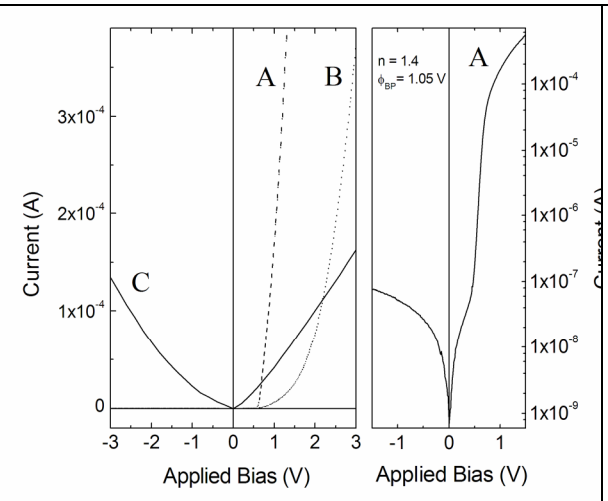

Figure 1: I-V characteristics for Al-diamond(001) contacts: (A) measured in ultra-high vacuum, (B) measured in air and (C) heated to 1100 K and measured in air.

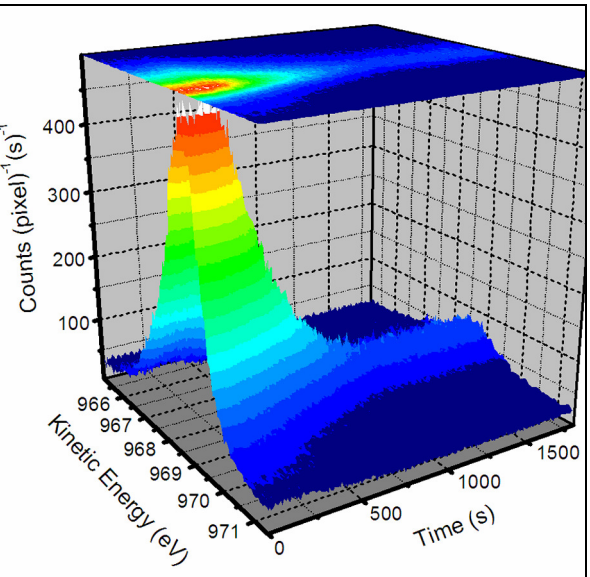

Figure 2: C1s photoelectron emission spectra recorded in snapshot mode for Al contact growth on a p-type diamond (001) surface.

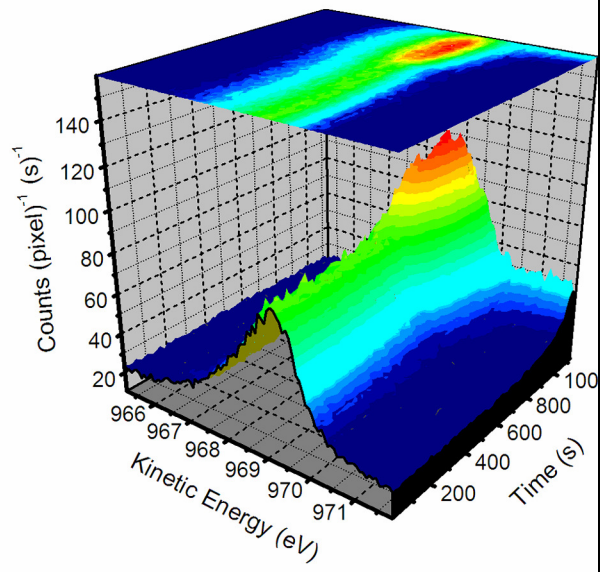

Figure 3: C1s photoelectron emission spectra recorded in real-time during in-situ annealing of an Al contact on a p-type diamond (001) surface.

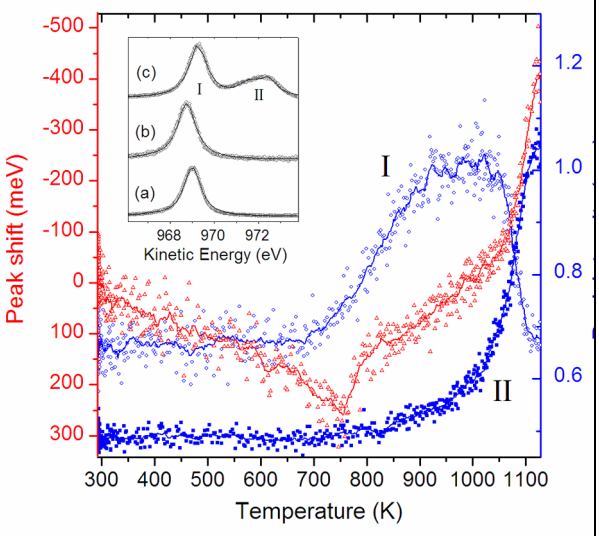

Figure 4: C1s peak intensities for the diamond (I – open circles) and carbide (II – filled squares) and the diamond peak shift (I – open triangles) as a function of temperature. The inset shows C 1s spectra for the clean surface (a), the metallized surface (b) and the annealed metallized surface (c).